



Degradation of Biebrich Scarlet Textile Dye by using MBIR Dowex-1x8

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ABSTRACT

In the present study, Methylene blue immobilized resin (MBIR) Dowex-1x8, an effective heterogeneous photocatalyst, is used to perform the photocatalytic degradation of Biebrich Scarlet (BS) Textile dye. The degradation of the dye was systematically investigated under different parameters such as pH of the Biebrich Scarlet dye solution, different Photocatalyst doses, dye solution concentrations, and UV/Visible light intensity. Optimum results are shown for various parameters, such as temperature of 30°C, pH of 7.5, photocatalyst loading dose of 2.0 g, and light intensity of 10.5mW/cm². Maximum degradation is shown on the above optimum condition and complete degradation was held in 210 minutes on the above optimum condition.

Keywords: Photocatalyst, Immobilization, Biebrich Scarlet dye, Methylene Blue, Optical density, Photodegradation, Dowex-1x8

INTRODUCTION

The dyes are used in industries at different scales, such as textiles, paints, inks, plastics, cosmetics, etc. These are creating environmental problems. Dye is mainly used in the clothing industry¹⁻². In many countries, regulations have been adopted to discharge dye-containing dyed effluents. Azo dyes are the most prevalent dyes produced chemically. Azo dyes, including the dyes of the Biebrich Scarlet (BS), are particularly problematic due to their high prevalence. It is used in textiles (wool, silk, and cotton) where bright colours with a fluorescent effect are needed. Biebrich Scarlet is a common anionic azo dye. Biebrich Scarlet dyes include two groups of -N=N-, two groups of sulphonate (SO₃⁻), and two

sodium atoms³⁻⁴. The dye is non-biodegradable, its by-products are highly toxic, and poses a danger to human health and aquatic life⁵. Active carbon adsorption and chemical coagulation are commonly used to treat such dyes. However, these methods only transfer water dyes to solids, and the ideal solution requires additional treatment⁶⁻⁸.

Dyeing is a fundamental operation in textile fiber processing that result in the production of colored wastewater. Thus, the use and disposal of textiles and other industrial effluent is an important consideration in assessing the environmental impact of textile manufacturing. In the Textile industry, different types of dyes are used, in which azo dyes are the most common type of dye that contains an



azo group (-N=N-)⁹. Textile effluent can be removed using physical and chemical methods such as absorption, precipitation, air removal, reverse osmosis, ultrafiltration, and flocculation. Hence, the need to create chemical treatments that are more successful at removing colors from wastewater¹⁰⁻¹⁵.

Applying advanced oxidation processes (AOPs) to totally remove colors has recently received much attention. AOPs works by producing reactive species such as OH radical, which have quick and no selective oxidation for various organic pollutants¹⁶⁻²⁰. AOPs include photocatalysis system, such as semiconductor and oxidant combinations as well as semiconductor and light combinations. The majority of organic pollutants, including organic reactive colors, have been completely mineralized as a result of heterogeneous photo catalysis, which has become a significant destructive technique²¹⁻²⁵. Supported photo catalysts have been developed as a solution to this issue. To efficiently use solar energy, the UV/Visible light induced photocatalyst MBIR Dowex-11 has completed a phenomenal success²⁶.

The MBIR Dowex-1x8 photocatalysts has been developed as a solution to this issue^{27,28}. To our knowledge, no one has reported the photocatalytic degradation of the MBIR Dowex-1x8 dye to Biebrich Scarlet. Taking all the above factors into the account, the present study reported that it utilized photocatalytic Methylene Blue Immobilized Resin (MBIR) Dowex-1x8 with optimum values of various parameters affecting the degradation of Biebrich Scarlet dye. The dose of the photocatalyst, the pH, and the initial concentration of the sample has been analyzed.

MATERIALS AND METHODS

The dye Biebrich Scarlet purchased from Loba chemie (India), the photocatalyst Dowex-1x8 resins, 20-50 mesh size (Sisco chem) and Methylene blue hydrate (Loba chemie, India). The different solution was prepared in the double distilled water. The desired pH conditions were adjusted using standardized solutions of 1N NaOH and 1N H₂SO₄. The pH of the prepared solution is determined with the help of a digital pH meter. All experiments were conducted at ambient temperature with magnetic stirrer. The structure (Fig. 1) and properties of Biebrich Scarlet dye are given in Table 1.

Table 1: Properties of Biebrich Scarlet (BS) dye

Dye Name	:	Biebrich Scarlet(BS)
C.I. Name	:	Acid Red 66
C.I. No.	:	26905
Other Name	:	Croceine Scarlet
Molecular Formula	:	C ₂₂ H ₁₄ N ₄ O ₇ S ₂ Na ₂
Molecular Weight	:	556.5gm/mol
Class	:	Azo Dye
Nature	:	Acidic
λ_{max}	:	507 nm

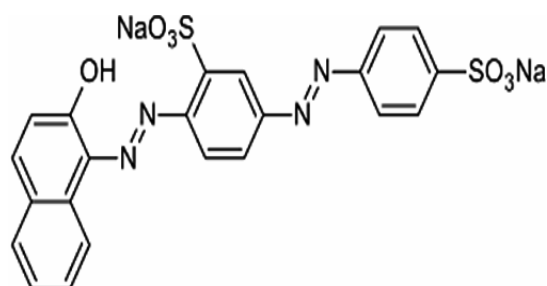


Fig. 1. Structure of Biebrich Scarlet dye

Preparation of photocatalyst

The photocatalyst is prepared from Dowex-1x8 resin, 20-50 mesh sizes, and Methylene Blue hydrate. To immobilize, prepare the Methylene Blue hydrate solution in a concentration of M/100 in distilled water, add the Dowex-1x8 resin to the solution, and shake it well, immobilizing the spores for at least 24 hours. After this the solution is kept stable in a dark place. Then the prepared immobilized resin is filtered and used as a photo catalyst by washing thoroughly with double distilled water 2-3 times.

Purpose of Methylene Blue

Methylene Blue (MB) is a cationic photosensitive dye. Particles of MB are present in the pores of the immobilized resin. The excitation of MB dyes molecules by absorbing photons of light from radiation. When the photon falls, the electrons are excited and move from the electronic transition valence band (VB) to the conduction band (CB), allowing the electrons of Methylene blue to go from a single state to a triplet state via inter-system crossing (ISC). This study shows that the formation of •OH radical and superoxide ion (O₂⁻) in the pores of the immobilization resin, they are highly oxidative in nature.

Experimental setup and degradation process

Photodegradation experiments have been conducted in a glass reactor that contains a solution of Biebrich Scarlet dye and a photocatalyst.

The solution is continuously stirred with the help of magnetic stirrer during the experiment. The solution is lit above the reactor with a 200-watt tungsten lamp (Indian Philips) and emits visible light-like radiation (Fig. 2). The radiation lamp was surrounded by Aluminum reflectors to avoid any radiation loss. The mechanism of photocatalytic degradation systems under UV/Visible light is the reaction of extremely active oxygen species and electron excitation technology, which primarily react with the dye molecules that cause photodegradation.

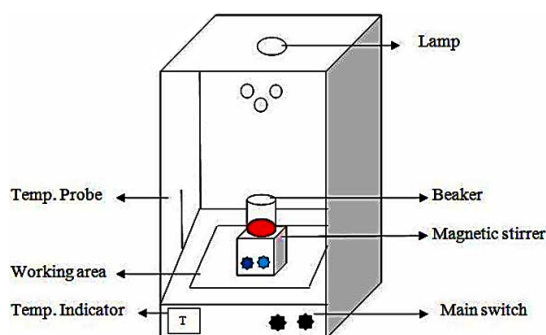


Fig. 2. Experimental Setup of Photoreaction chamber

Analytical approach

The change in dye concentration was observed by the CSIM 500 microprocessor UV/Visible spectrophotometer at max. We eject 5 mL solution by pipette a time interval of 10 min filter catalyst particles, record the absorbance spectrum of the dye solution and the rate of degradation was observed in terms of change in the light intensity at max of the dye. We calculated the degradation efficiency (%):

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

Where C_0 and C correspond to the initial and final concentrations of BS dye before and after photo irradiation.

So the above formula is related to the absorbance of BS dye (concentration). According to the concept of literature, absorbance is directly proportional to concentration. In this calculation, we are using absorbance with respect to the BS dye concentration. Absorbance is the quantity of light absorbed by a solution, also known as optical density.

Time	Optical density	Degradation efficiency %
0	1.078	0
10	0.809	24.96
20	0.672	37.66
30	0.552	52.66
40	0.471	56.31
50	0.412	61.78
60	0.361	66.51
70	0.316	70.68
80	0.279	74.11
90	0.238	77.92
100	0.204	81.07
110	0.167	83.81
120	0.144	86.64
130	0.118	89.05
140	0.098	90.91
150	0.073	93.22
160	0.051	95.26
170	0.038	96.47
180	0.032	97.03
190	0.028	97.41
200	0.025	97.68
210	0.023	97.96

RESULT AND DISCUSSION

Effect of Photocatalyst amount

The amount of the photocatalyst affects the rate of photocatalytic degradation of BS dye. We find out change in the amount (from 1.0 g to 2.5 g) of photocatalyst on the rate of degradation at constant other parameters. We observed that as the amount of photocatalyst increases, the rate of degradation of BS dye also increases. The amount of photocatalyst is increases due to the availability of more surface area for the absorption of photons and the cooperation of molecules in the reaction mixture with the photocatalyst. The outcome is that the number of oxidizing intermediate species (holes, $\bullet\text{OH}$ radicals, and O_2^- ions) increased, which increased the rate of degradation. In Fig. 3 the graph between optical density and Time shows that the photocatalytic amount on degradation rate.

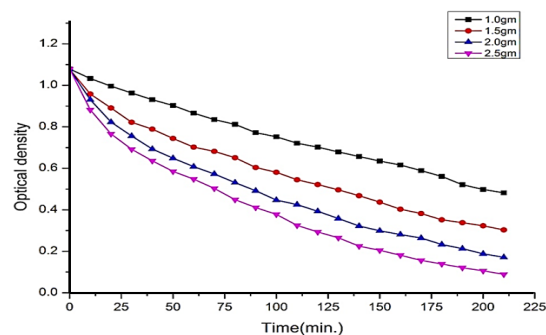


Fig. 3. Effect of photocatalyst amount on optical density

Effect of pH

We found that the variation in pH of BS dye solution, the degradation rate of dye molecules is very interesting for us. The outcome shows that in highly acidic pH range below pH 5, the degradation rate is very slow. When the pH of the solution is highly basic, the rate of degradation increases rapidly, and the pH range from 7.3 to 11, the rate of degradation is very good. At a constant photocatalytic amount 2.0 g/100 mL, BS dye concentration 30 mg/L, and light intensity 10.5mWcm⁻², the rate of degradation begins to increase as pH increases. As a result, we concluded that the degradation rate of BS dye in highly basic medium is higher than that of the acidic medium. The increase in photocatalytic degradation is due to the increased availability of •OH radical in the pH range of 7.3 to 11. The formation of more hydroxyl radicals (•OH) that combine with holes formed by electronic excitation in photocatalysts. Super oxides (O₂⁻) are less likely to cause photocatalytic degradation than hydroxyl radicals. As pH increases above 11, the degradation rate slows down. This effect may be caused by competition between •OH radicals and O₂⁻ for attachment to the active site of the photocatalyst. A graphical representation of the pH effect on the rate of degradation is shown in Figure 4.

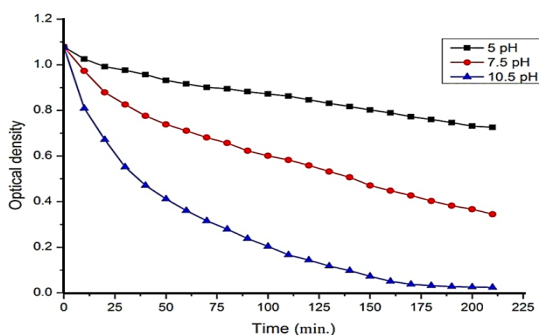


Fig. 4. Effect of solution pH on Optical density

Effect of initial BS dye Concentration

The degradation rate has been studied by varying the initial Biebrich Scarlet dye concentration from 10 to 50 mg/L based on a constant photocatalyst (2.0 g/100 mL), pH 7.5, and light intensity 10.5mWcm⁻². As the dye concentration increases, the rate of degradation decreases (shown in Fig. 5). The effect that may be caused by the degradation rate is due to the following reasons: the reduction in the number of photons striking the photocatalyst surface due to the increase in the dye concentration, and the

reduction in the number of photocatalyst molecules by excitation. As a result, the rate of formation of •OH radical and super oxide ion (O₂⁻) is reduced, also the rate of degradation is reduced. Because a limited amount of dye molecules is attached to the activated site of the photocatalyst and the remaining dye molecule remains present in solution until the previously attached molecule are degrade, the number of activated sites of the photocatalyst also decreases because of the excitation of the photocatalyst molecule. Less number of Photons is available at higher concentrations; the number of dye molecules is also greater, leading to greater competition between dye molecules attached to the activated photocatalyst site, thereby reducing the degradation rate.

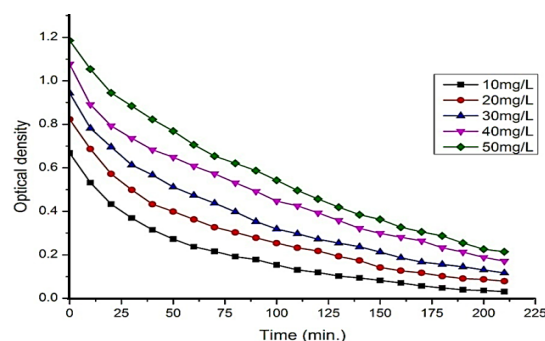


Fig. 5. Effect of initial BS dye concentration on optical density

Effect of UV/Visible light intensity

We observed the variation of light intensity on the rate of degradation. We conclude that if the light intensity increases, degradation rate of BS dye molecules increases to a lap of time, and after that time, invariable in the degradation rate of the dye is observed at that light intensity. This change in degradation rate of the dye molecule is due to the change in intensity of the light. As the intensity of light increases (from 5.4 mWcm⁻² to 15.5 mWcm⁻²), the number of photons reaching at the surface of the photocatalyst increases, the number of pores, hydroxyl radical (•OH), and super oxide ions (O₂⁻) increases, and the degradation rate of dye molecules increases. This can result in the availability of the maximum number of photons required for the excitation within a constant range of photon light intensity after a significant change in the rate of degradation is observed because the excitation does not require more photons. Since all photocatalyst molecules are active in fixed light intensity ranges, the degradation rate remains unchanged when light intensity increases to any range (Figure 6).

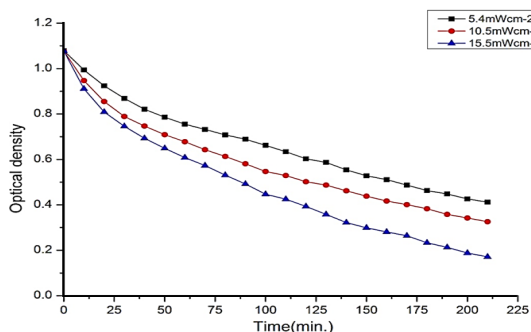


Fig. 6. Effect of visible light intensity on optical density

FTIR Analysis of BS Dye

FTIR plot (a, before degradation of dye) and (b, after degradation of dye) shows the comparative study of before and after the degradation of BS azo dye. In the plot (a) show IR frequencies of azo bond lie in between $1500\text{--}1600\text{ cm}^{-1}$ (Alica Bartosova *et al.*, 2017)²⁹. But in the plot (b), there is no peak observed in between $1500\text{--}1600\text{ cm}^{-1}$. So below IR frequencies data shows that there is no azo bond is present after the degradation of BS dye. In Fig. 7 graph (b) show the IR study for the degradation of BS dye.

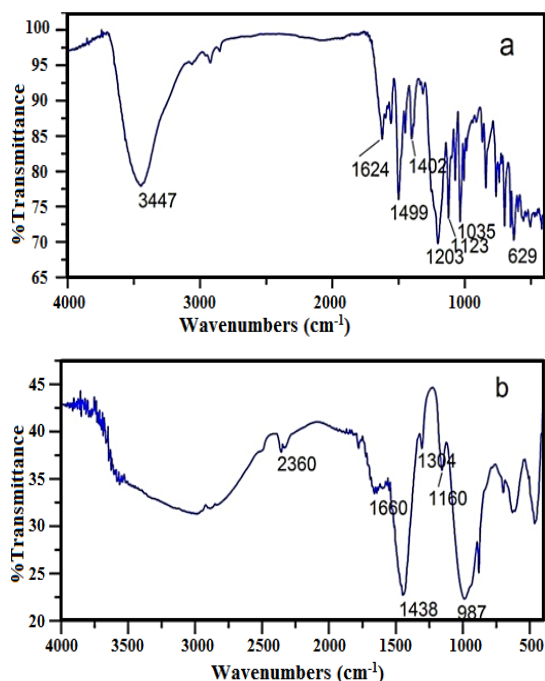


Fig. 7. FTIR analysis for BS dye (a) Before degradation, (b) After degradation

CONCLUSION

This study focuses on the evaluation of Biebrich Scarlet dye degradation with an

MBIR Dowex-1x8. The system operates under different conditions (dye concentrations, amounts of photocatalyst, light intensities, pH). The change in the transparency of the solution from a colored dye solution to a transparent solution reflects the favorable outcome of the practical setup of the devices in implementing the MBIR Dowex-1x8 photocatalyst. The maximum degradation efficiency 98% is obtain at optimum condition (dye concentration 30 mg/L, amount of photocatalyst 2.0 g/100 mL, light intensity 10.5mWcm^{-2} , pH 10.5) These result shows that the new reactor setup using MBIR Dowex-1x8 photo catalysis textiles industry provide a prominent technology for improving the standard of wastewater from effluent degradation plants. We conclude, this photocatalyst (MBIR dowex-1x8) has a high ability to degrade simple azo dye molecules and purify textile effluent containing high levels of dye (mostly azo dyes) after extensive testing. We looked at the effects of different parameter:

- Variation of dye concentrations: As the dye concentrations increase, dye degradation rates decrease.
- Variation in the amount of photocatalyst: As the amount of the photocatalyst increases, the degradation rate of dye is also increases.
- Change in pH: The degradation rate is very low in the acidic medium, but in the basic medium, the degradation rate is high.
- Variation in Intensity of light: The degradation rate of dye molecule increases to a particular extent as the light intensity increases, and there is no further change in the degradation rate after that.
- FTIR analysis of the degraded dye solution using immobilized Dowex-1x8 is carried out after a photo degradation process of 210 min. The dye was completely degraded in MBIR dowex-1x8, and no azo bonds were detected in the degraded dye. The decolorizing of the solution was due to degradation.

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Conflict of interest

The author declare that we have no conflict of interest.

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